Olin

PROPOSED

STUDY PLAN AND INVESTIGATION

OLIN CORPORATION

McINTOSH, ALABAMA

OLIN BASIN

Environmental Affairs Department

3 4 00002

PROPOSED
STUDY PLAN AND INVESTIGATION
OLIN CORPORATION
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OLIN BASIN

TABLE OF CONTENTS

3 4 00004

SAMPLE LOCATIONS

I. WATER

Sample for water at eight locations as shown on Olin Drawing No. SKD-10-10-38. The locations, described below, were selected on the basis of:

(1) Relationship to basin discharge

(2) Relationship to original effluent ditch location

(3) Overall coverage of pond

A. Current effluent ditch below Basin discharge including current effluent and Basin discharge.

B. Old effluent ditch into Basin

C. North shallow area adjacent to old effluent ditch into Basin

D. South shallow area adjacent to old effluent ditch into Basin

E. North Basin area

F. East Basin area

G. North and South deep areas

II. SEDIMENT

Sample for sediment at ten locations as shown on Olin Drawing No. SKD-00-10-39. The locations, described below, were selected on the basis of:

(1) Relationship to Basin discharge

(2) Relationship to original effluent ditch location

(3) Relationship to possible sediment deposition

(4) Overall coverage of pond

A. Current effluent ditch below Basin discharge including current effluent and Basin discharge.

B. Old effluent ditch into Basin

C. North shallow area adjacent to old effluent ditch into Basin

D. South shallow area adjacent to old effluent ditch into Basin

E. North Basin area

F. East Basin area

G. North and South deep water areas

H. North grass area adjacent to old effluent ditch into Basin

I. South grass area adjacent to old effluent ditch into Basin

III. GENERAL

As stated above, the eight water sample locations will also be sampled for sediment. To minimize disturbance to these sample locations, the following procedure will be followed:

1) Measure depth of water
2) Take water sample(s) - see Sampling Methodology Section
3) Mark sampling point with buoy
4) Wait minimum of 24 hours
5) Take sediment samples - see Sampling Methodology Section

Specific sampling points for deep water, North Basin and East Basin will be selected in the field predicated on water depth, sediment depth and field accessibility. Actual sampling location could vary by ±300 feet from that shown on Olin Drawing SKD-10-10-38 and SKD 10-10-39.

Actual sampling points will be marked on Topographic Map which will be submitted with the final report (see Investigation Report Section).

PARAMETERS

Olin has selected five analytical parameters that all samples will be checked for. They are as follows:

1) Mercury
2) 1,2-Dichlorobenzene (orthodichlorobenzene)
3) 1,4-Dichlorobenzene (paradichlorobenzene)
4) Hexachlorobenzene (HCB)
5) Pentachloronitrobenzene (PCNB)

Water samples will be analyzed for total mercury while sediment samples will be analyzed for total and EP extractable mercury.

Mercury

Mercury was selected as a parameter for two major reasons. First, Olin operated a Mercury Cell Chlorine/Caustic Soda plant at McIntosh from 1952 through 1982. Second, Olin discharged the NPDES wastewater from the Mercury Cell plant into the Basin until 1976.

1,2 and 1,4 - Dichlorobenzene

1,2 and 1,4 - Dichlorobenzene (the ortho and para isomers) were selected as parameters because they were a waste product of the Crop Protection Chemical (CPC) facility at McIntosh. Also, they are in the groundwater that the Groundwater Corrective Action Plan (USEPA RCRA Post-Closure Permit No. ALD008188708) is directed at cleaning up.

Hexachlorobenzene

Hexachlorobenzene was selected because it was also a waste product of the CPC facility at McIntosh. Blocks of Hexachlorobenzene were used for erosion control on the edges of the plant's main East-West ditch and in the effluent ditch approximately ½ mile east of the main plant. Both ditches are part of the NPDES effluent system. All hexachlorobenzene in these ditches was removed in 1977.

Pentachloronitrobenzene

From 1956 until 1982, one of the main products of the CPC facility was Pentachloronitrobenzene. As a condition of NPDES permit (No. AL0001945), Olin was required to sample, analyze and report on the discharge when the facility was operating.

DOCUMENTATION

Olin will meet or exceed the documentation requirements for the sampling and analysis of the Basin as specified in Test Methods for Evaluating Solid Waste, SW-846, July 1982, USEPA, Second Edition.

Specifically, Olin's program consists of three parts: (1) Field Log Book, (2) Sample Seals and Labels and (3) Chain-of-Custody Records.

Field Log Book

A Field Log Book (hard cover or spiral notebook) with prenumbered pages will be kept to record all information pertinent to the sampling. A a minimum, the following will be entered:

1) Date
2) Observable weather conditions (sunny, cloudy, etc.)
3) Observable Basin condition (clear, muddy, etc.)
4) Sampling team members names
5) Sample location
6) Sample type (water, sediment)
7) Water depth, temperature, pH
8) Description of sampling point
9) Time sample collected

10) Sample number

11) Number and volume of samples taken

12) Sampling methodology

13) Field Preservation, if any

14) Sample distribution and how transported

15) Signatures of sampling team members

In addition, records of conversation, if any, between Olin and the analytical laboratory will be documented in the Field Log Book.

Sample Seals and Labels

To prevent misidentification of samples, gummed paper labels will be affixed to each sample bottle by the laboratory which will include the following information:

1) Sample number (prenumbered by the analytical laboratory)

2) Sample identification

3) Sample type

4) Name of collector

5) Date and time of collection

6) Place of collection

7) Analysis required

8) "Olin Corporation, McIntosh, Alabama"

In addition, each bottle will be sealed in such a way that it is necessary to break the seal to open the sample container.

Chain-of-Custody Records

To establish and maintain the documentation necessary to trace sample possession from the time of collection through analysis, a Chain-of-Custody Record will be filled out and accompany every sample. Olin-McIntosh will use its standard Chain-of-Custody Record form which is attached in Section VIII. Completed copies of the record will be requested from the analytical laboratory to accompany their final report. The completed Chain-of-Custody records will then be appended to the Field Log Book.

SAMPLING METHODOLOGY

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Detailed below are the specific sampling methodologies and sample preservations that will be used to collect the water and sediment samples. All samples will be taken in duplicate (including the field blanks) to insure delivery of an undisturbed sample. Only one of each sample will be analyzed. It is estimated that the water samples can be taken in 1-2 days depending upon weather conditions and accessibility and that the sediment samples can be taken in 2-3 days.

Water Sampling

1) Measure depth of water using weighted measuring tape, measuring pole or similar device.

2) Measure pH of water using Method 150.1 from Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1979, USEPA (copy attached in Section VIII).

3) Measure temperature of water using Method 170.1 from Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1979, USEPA (copy attached in Section VIII).

4) If the depth of the water is less than three (3) feet, a single sample using the Weighted Bottle Method (Test Methods for Evaluating Solid Waste, SW-846, USEPA, July 1982, Second Edition, Implementation of Sampling Plan, pg. 7 Method 1.2.1.2 Weighted Bottle - copy attached in Section VIII) will be taken at 0.6 times the depth.

5) If the depth of water is greater than three (3) feet, two samples will be taken using the Weighted Bottle Method (ibid): (1) at 0.2 times the depth, and (2) at 0.8 times depth.

Sediment Sampling

1) Measure temperature of water using Method 170.1 from Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1979, USEPA (copy attached in Section VIII).

2) Measure pH of water using Method 150.1 from Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1979, USEPA (copy attached in Section VIII).

3) A Phleger Corer or similar device (Standard Methods for the Examination of Water and Wastewater, Sixteenth Edition, 1985 American Public Health Association, pg. 1121, "c. Core or Cyclindrial Samplers" - copy attached in Section VIII) will be used to obtain a 0-6" sediment sample. The coring device will be washed with Basin water after each sample is taken.

Sample Preservation and Collection

Sample bottles and preservation of individual samples will be pursuant to the requirements for each parameter's specific methodology in Test Methods for Evaluating Solid Waste, SW-846, USEPA, July 1982, Second Edition. Briefly these are:

1) Mercury - Water: Sampled and stored in glass containers. Samples will be acidified to a pH of less than 2.0 with nitric acid. Samples will be iced or refrigerated from the time of sampling until analysis. Samples will be analyzed within 38 days of collection.

2) Mercury - Sediment: Samples stored in glass containers. Samples will be iced or refrigerated from the time of sampling until analysis. Samples will be analyzed within 40 days of collection. Samples will be dried in an oven at a temperature of 60°C.

3) Ortho and para dichlorobenzene, pentachloronitrobenzene and hexachlorobenzene - Water and Sediment: Samples will be taken in glass containers with Teflon-lined screw caps. Samples will be iced or refrigerated at 4°C from the time of sampling until extraction. Samples will be extracted within 14 days of collection and analyzed within 40 days of extraction.

ANALYTICAL METHODOLOGY

An outside contract laboratory will be selected by Olin to analyze the samples based on the laboratory's overall analytical capability, capability to analyze for the required parameters and familiarity with Olin-McIntosh samples. The laboratory will be required to follow (and document to Olin) all USEPA procedures for the specified methodologies. The laboratory will be required to supply Olin with all sampling bottles, shuttles and trip blanks.

All analysis will be performed pursuant to:

1) Test Methods for Evaluating Solid Waste, SW-846, USEPA, July 1982, Second Edition - hereafter referred to as "SW-846" or,

2) Standard Methods for the Examination of Water and Wastewater, Sixteenth Edition, 1985, American Public Health Association - hereafter referred to as "Standard Methods" or,

3) 40 CFR 261 Appendix II - EP Toxicity Test Procedure (Revised 46 FR 35247, July 7, 1981) hereafter referred to as "EP Extract"

All sediment samples will be split at the laboratory. One split will be run for the specified analysis detailed below and the second split will be run for Percent Moisture and Specific Gravity. The Standard Methods will be used for Moisture and Specific Gravity using Method 209A. "Total Solids Dried at

103-105°C" (pg. 93) and Method 213E. "Specific Gravity" (pg. 132) respectively or equivalent methods approved by Olin: copies of the methods are attached in Section VIII. Results of all sediment samples will be reported on a dry weight basis.

Water samples for mercury will be analyzed using SW-846 Method 7470 (attached Section VIII). Sediment samples for mercury will be run using SW-846 Method 7471 (attached Section VIII) for total mercury and EP Extract for leachable mercury.

Analysis for ortho and para dichlorobenzene, hexachlorobenzene and pentachloronitorbenzene will be done using SW-846 Method 8250 GC/MS Method for Semivolatile Organics: Placed Column Technique (attached Section VIII) or equivalent method approved by Olin prior to use.

QUALITY ASSURANCE/QUALITY CONTROL

The outside laboratory will be required to supply a trip blank (in duplicate to insure sample integrity) in each sample shuttle supplied to Olin. Olin will supply a field blank (in duplicate to insure sample integrity) in each sample shuttle returned to the laboratory. The blanks will be run for total mercury, ortho and para dichlorobenzene, hexachlorobenzene and pentachloronitrobenzene using the methods specified in the Analytical Methodology Section.

Two blind replicates for water and two blind replicates for sediment (both in duplicate to insure sample integrity) will also be sent to the laboratory for the specified parameters. This represents approximately a 20% replicate analysis.

All water and sediment samples being analyzed for ortho and para dichlorobenzene, hexachlorobenzene and pentachlorobenzene will be spiked and recoveries determined. In addition, the laboratory will spike and recover each water and sediment sample with a surrogate. Olin recommends 1,3-dichlorobenzene as the surrogate. This is a 100% spike and recovery quality assurance check.

Splits from two water and two sediment samples will also be spiked and recovery of total mercury determined. The splits will utilize analytical methodology, SW-846 Method 7470 and 7471 for water and sediment respectively. This represents approximately a 20% spike and recovery.

The outside laboratory will be required to supply Olin with their QA/QC program that at a minimum meets SW-846 Section Ten, Method 7470, Method 7471 and Method 8250 requirements. The laboratory will also supply Olin with their minimum detection levels that at least meet EPA Laboratory Guidelines for all parameters and surrogates.

In addition, the laboratory will supply Olin with their QA/QC data and results for the days that analysis of Olin samples are run. This will include all gas chromatograms of Olin samples, replicates, blanks, spikes and the daily laboratory QA/QC data.

INVESTIGATION REPORT

Olin will prepare and submit a report to the USEPA on the investigation within 8 weeks of receipt and review of the analytical data. The report will include: a summary of the sampling program including any significant field notes and a map showing the exact sampling locations; complete analytical results including QA/QC data; an evaluation of the analytical results; and conclusions based upon the investigatory program. The conclusions will include recommendation for further work if necessary.

ALF/wsr

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ATTACHMENTS

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1. Chain-of-Custody Record
2. Method 150.1 pH - Electrometric
3. Method 170.1 Temperature
4. Method 1.2.1.2 Weighted Bottle
5. c. Core or Cyclindrical Samplers
6. Method 209A. "Total Solids Dried at 103-105°C"
7. Method 213E. "Specific Gravity"
8. Method 7470 Mercury (Manual Cold-Vapor Technique)
9. Method 7471 Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique)
10. Method 8250 GC/MS Method for Semivolatile Organics in Packed Column Technique

009/ALF5

Olin CHEMICALS

McINTOSH PLANT — McINTOSH, ALABAMA 36553 (205) 944-2231

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CHAIN OF CUSTODY RECORD

Sample Location	Time	pH	# Containers	Remarks

Collector's Name _____ Date of Collection _____
(Signature)

SAMPLE RECEIVERS:

1. _____
(Name and address of organization receiving sample)
2. _____
3. _____

CHAIN OF POSSESSION:

(Signature of collector) (Title) (Inclusive dates/times)

Remarks: _____

1. (Signature) (Title) (Inclusive dates/times)

Remarks: _____

2. (Signature) (Title) (Inclusive dates/times)

Remarks: _____

3. (Signature) (Title) (Inclusive dates/times)

Remarks: _____

pH

Method 150.1 (Electrometric)

STORET NO.
Determined on site 00400
Laboratory 00403

1. Scope and Application
   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
2. Summary of Method
   2.1 The pH of a sample is determined electrometrically using either a glass electrode in combination with a reference potential or a combination electrode.
3. Sample Handling and Preservation
   3.1 Samples should be analyzed as soon as possible preferably in the field at the time of sampling.
   3.2 High-purity waters and waters not at equilibrium with the atmosphere are subject to changes when exposed to the atmosphere, therefore the sample containers should be filled completely and kept sealed prior to analysis.
4. Interferences
   4.1 The glass electrode, in general, is not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants or high salinity.
   4.2 Sodium error at pH levels greater than 10 can be reduced or eliminated by using a "low sodium error" electrode.
   4.3 Coatings of oily material or particulate matter can impair electrode response. These coatings can usually be removed by gentle wiping or detergent washing, followed by distilled water rinsing. An additional treatment with hydrochloric acid (1 + 9) may be necessary to remove any remaining film.
   4.4 Temperature effects on the electrometric measurement of pH arise from two sources. The first is caused by the change in electrode output at various temperatures. This interference can be controlled with instruments having temperature compensation or by calibrating the electrode-instrument system at the temperature of the samples. The second source is the change of pH inherent in the sample at various temperatures. This error is sample dependent and cannot be controlled, it should therefore be noted by reporting both the pH and temperature at the time of analysis.
5. Apparatus
   5.1 pH Meter-laboratory or field model. A wide variety of instruments are commercially available with various specifications and optional equipment.

Approved for NPDES
Issued 1971
Editorial revision 1978

5.2 Glass electrode.

5.3 Reference electrode–a calomel, silver-silver chloride or other reference electrode of constant potential may be used.

NOTE 1: Combination electrodes incorporating both measuring and reference functions are convenient to use and are available with solid, gel type filling materials that require minimal maintenance.

5.4 Magnetic stirrer and Teflon-coated stirring bar.

5.5 Thermometer or temperature sensor for automatic compensation.

6. Reagents

6.1 Primary standard buffer salts are available from the National Bureau of Standards and should be used in situations where extreme accuracy is necessary.

6.1.1 Preparation of reference solutions from these salts require some special precautions and handling[1] such as low conductivity dilution water, drying ovens, and carbon dioxide free purge gas. These solutions should be replaced at least once each month.

6.2 Secondary standard buffers may be prepared from NBS salts or purchased as a solution from commercial vendors. Use of these commercially available solutions, that have been validated by comparison to NBS standards, are recommended for routine use.

7. Calibration

7.1 Because of the wide variety of pH meters and accessories, detailed operating procedures cannot be incorporated into this method. Each analyst must be acquainted with the operation of each system and familiar with all instrument functions. Special attention to care of the electrodes is recommended.

7.2 Each instrument/electrode system must be calibrated at a minimum of two points that bracket the expected pH of the samples and are approximately three pH units or more apart.

7.2.1 Various instrument designs may involve use of a "balance" or "standardize" dial and/or a slope adjustment as outlined in the manufacturer's instructions. Repeat adjustments on successive portions of the two buffer solutions as outlined in procedure 8.2 until readings are within 0.05 pH units of the buffer solution value.

8. Procedure

8.1 Standardize the meter and electrode system as outlined in Section 7.

8.2 Place the sample or buffer solution in a clean glass beaker using a sufficient volume to cover the sensing elements of the electrodes and to give adequate clearance for the magnetic stirring bar.

8.2.1 If field measurements are being made the electrodes may be immersed directly in the sample stream to an adequate depth and moved in a manner to insure sufficient sample movement across the electrode sensing element as indicated by drift free (< 0.1 pH) readings.

8.3 If the sample temperature differs by more than 2°C from the buffer solution the measured pH values must be corrected. Instruments are equipped with automatic or manual

[1]National Bureau of Standards Special Publication 260.

compensators that electronically adjust for temperature differences. Refer to manufacturer's instructions.

8.4 After rinsing and gently wiping the electrodes, if necessary, immerse them into the sample beaker or sample stream and stir at a constant rate to provide homogeneity and suspension of solids. Rate of stirring should minimize the air transfer rate at the air water interface of the sample. Note and record sample pH and temperature. Repeat measurement on successive volumes of sample until values differ by less than 0.1 pH units. Two or three volume changes are usually sufficient.

9. Calculation

9.1 pH meters read directly in pH units. Report pH to the nearest 0.1 unit and temperature to the nearest °C.

10. Precision and Accuracy

10.1 Forty-four analysts in twenty laboratories analyzed six synthetic water samples containing exact increments of hydrogen-hydroxyl ions, with the following results:

pH Units	Standard Deviation pH Units	Accuracy as Bias, %	Accuracy as Bias, pH Units
3.5	0.10	-0.29	-0.01
3.5	0.11	-0.00	
7.1	0.20	+1.01	+0.07
7.2	0.18	-0.03	-0.002
8.0	0.13	-0.12	-0.01
8.0	0.12	+0.16	+0.01

(FWPCA Method Study 1, Mineral and Physical Analyses)

10.2 In a single laboratory (EMSL), using surface water samples at an average pH of 7.7, the standard deviation was ±0.1.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 460, (1975).
2. Annual Book of ASTM Standards, Part 31, "Water", Standard D1293-65, p 178 (1976).

TEMPERATURE

Method 170.1 (Thermometric)

STORET NO. 00010

1. Scope and Application
   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
2. Summary of Method
   2.1 Temperature measurements may be made with any good grade of mercury-filled or dial type centigrade thermometer, or a thermistor.
3. Comments
   3.1 Measurement device should be routinely checked against a precision thermometer certified by the National Bureau of Standards.
4. Precision and Accuracy
   4.1 Precision and accuracy for this method have not been determined.
5. Reference
   5.1 The procedure to be used for this determination is found in:
   Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 125, Method 212 (1975).

Approved for NPDES
Issued 1971

Procedure

1. Clean Coliwasa.

2. Adjust sampler's locking mechanism to ensure that the stopper provides a tight closure. Open sampler by placing stopper rod handle in the T-position and pushing the rod down until the handle sits against the sampler's locking block.

3. Slowly lower the sampler into the waste at a rate that permits the level of liquid inside and outside the sampler to remain the same. If the level of waste in the sampler tube is lower inside than outside, the sampling rate is too fast and will produce a nonrepresentative sample.

4. When the sampler hits the bottom of the waste container, push sampler tube down to close and lock the stopper by turning the T-handle until it is upright and one end rests on the locking block.

5. Withdraw Coliwasa from waste and wipe the outside with a disposable cloth or rag.

1.2.1.2 Weighted Bottle

Scope and Application

This sampler consists of a glass or plastic bottle, sinker, stopper, and a line which is used to lower, raise, and open the bottle. The weighted bottle samples liquids and free-flowing slurries.

General Comments and Precautions

1. Do not use a nonfluorocarbon plastic bottle to sample wastes containing organic materials.

2. Do not use a glass bottle to sample wastes that contain hydrofluoric acid.

3. Before sampling, ensure that the waste will not corrode the sinker, bottle holder, or line.

Apparatus

A weighted bottle with line is built to the specifications in ASTM Methods D 270 and E 300. Figure 2 shows the configuration of a weighted bottle sampler.

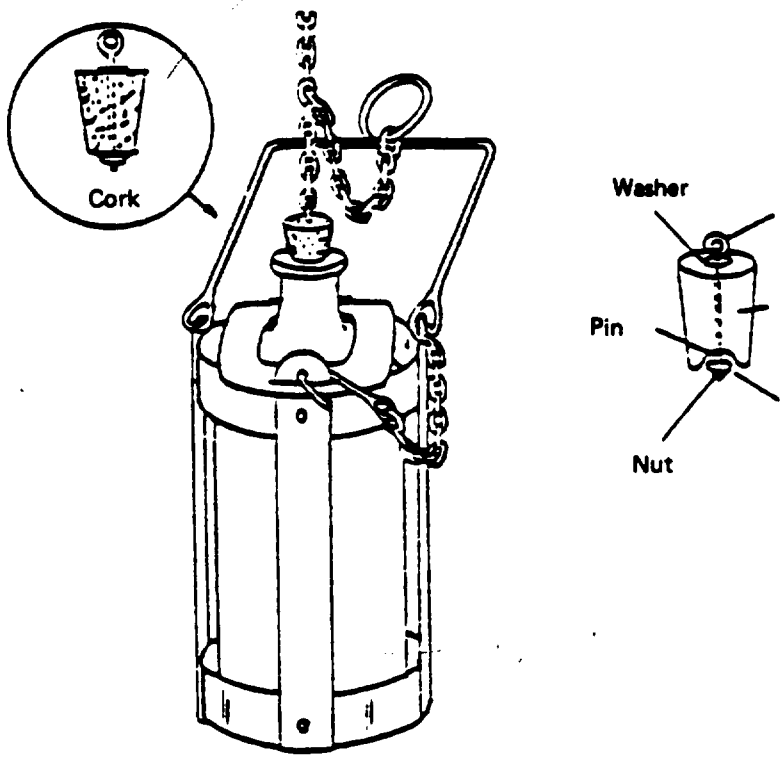

Figure 2. Weighted bottle sampler.

Procedure

1. Clean bottle.
2. Assemble weighted bottle sampler.
3. Lower the sampler to directed depth and pull out the bottle stopper by jerking the line.
4. Allow bottle to fill completely as evidenced by cessation of air bubbles.
5. Raise sampler, cap, and wipe off with a disposable cloth. The bottle can serve as a sample container.

1.2.1.3 Dipper

Scope and Application

The dipper consists of a glass or plastic beaker clamped to the end of a 2- or 3-piece telescoping aluminum or fiberglass pole which serves as the handle. A dipper samples liquids and free-flowing slurries.

General Comments and Precautions

1. Do not use a nonfluorocarbon plastic beaker to sample wastes containing organic materials.
2. Do not use a glass beaker to sample wastes of high pH or wastes that contain hydrofluoric acid.
3. Paint aluminum pole and clamp with a 2-part epoxy or other chemical-resistant paint when sampling either alkaline or acidic wastes.

Apparatus

Dippers are not available commercially and must be fabricated to conform to the specifications detailed in Figure 3. Table 3 lists the parts required to fabricate a dipper.

Procedure

1. Clean beaker, clamp, and handle.
2. Assemble dipper by bolting adjustable clamp to the pole. Place beaker in clamp and fasten shut.
3. Turn dipper so the mouth of the beaker faces down and insert into waste material. Turn beaker right side up when dipper is at desired depth. Allow beaker to fill completely as shown by the cessation of air bubbles.
4. Raise dipper and transfer sample to container.

band of flexible material to bottom edge of sampler to create a seal in rocky, uneven substrates. Make band of foam rubber or fine-textured synthetic sponge. Remove organisms that stick to foam and include in sample.

c. Core or cylindrical samplers: Use core or cylindrical samplers to sample sediments in depth. They are better than a Surber sampler when used in combination with sieving of fine sediments contained within the small sample area, 13 to 26 cm^2. Efficient use as surface samplers requires dense animal populations. Core samplers vary from hand-pushed tubes to explosive-driven and automatic-surfacing models.[10]

1) *The Phleger corer* (Figure 1005:8) is widely used. It operates on the gravity principle. Styles and weights vary among manufacturers; some use interchangeable weights that allow variations between 7.7 and 35.0 kg, while others use fixed weights weighing 41.0 kg or more. Length of core taken will vary with substrate texture.

2) *The KB core sampler* (Figure 1005:9) or a modification known as the Kajak-Brinkhurst corer, may be useful in obtaining estimates of the standing stock of benthic macroinvertebrates inhabiting soft sediments.[11]

3) *The Wilding or stovepipe sampler* (Figure 1005:10) is made in various sizes and with many modifications. It is especially useful for quantitatively sampling a bottom with dense, vascular plant growth. It may be used to sample vegetation, mud-water interface sediment, or most shallow stream substrates. Large volumes of vegetation, when sampled in this way, may require a great deal of time for laboratory processing.

d. Drift samplers:

Drift nets (Figure 1005:11) are anchored in flowing water for capture of macroinvertebrates that have migrated or have been dislodged from the bottom substrates into the current. Drift organisms are important to the stream ecosystem because they are prey for stream fish and thus should be considered in the study of fish populations. Drift organisms respond to pollutional stresses by increased drift from an affected area; therefore, drift is important in water-quality investigations, especially of spills of toxic materials. Drift also is a factor in recolonizing denuded areas and it contributes to recovery of disturbed streams.

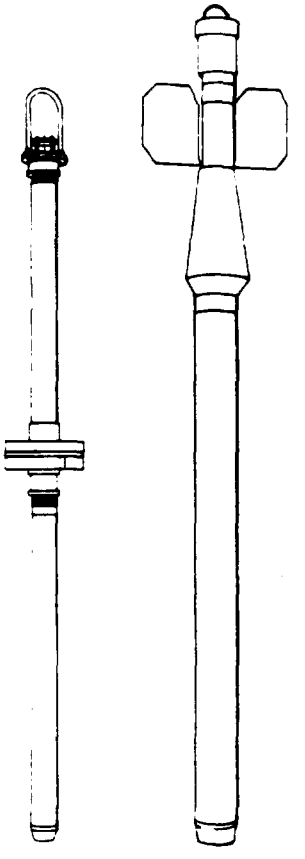

Figure 1005:8. Phleger core sampler.

Use nets having a 929-cm^2 upstream opening and mesh equivalent to U.S. Standard No. 30 screen (0.595-mm pore size). Alternatively, use a plastic net with a 0.471-mm pore size. After placing the net in the water, frequently remove organisms and debris to prevent clogging and subsequent diversion of water at the net opening.

ed. 1973. Compilation of Odor and reshold Values Data. Amer. Soc. Materials Data Ser. DS 48, Phil-Pa.
CIETY FOR TESTING AND MATE-'3. Annual Book of ASTM Stand-rt 23, D-1292-65, ASTM, ia, Pa.

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sample and its subsequent
en at a defined temperature.
:ludes "total suspended sol-
n of total solids retained by
total dissolved solids," the
ss; ough the filter.
fi der, the pore size,
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' is the term applied to the
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ed and volatile solids do
recisely between inorganic
er because the loss on ig-
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lue to decomposition or
ome mineral salts. Better
of organic matter can be
ts as total organic carbon
OD (Section 507), and
8).
ds" is the term applied to
ling out of suspension

within a defined period. It may include floating material, depending on the technique (209E.3*b*).

2. Sources of Error and Variability

The temperature at which the residue is dried has an important bearing on results, because weight losses due to volatilization of organic matter, mechanically occluded water, water of crystallization, and gases from heat-induced chemical decomposition, as well as weight gains due to oxidation, depend on temperature and time of heating.

Residues dried at 103 to 105°C may retain not only water of crystallization but also some mechanically occluded water. Loss of CO_2 will result in conversion of bicarbonate to carbonate. Loss of organic matter by volatilization usually will be very slight. Because removal of occluded water is marginal at this temperature, attainment of constant weight may be very slow.

Residues dried at 180 ± 2°C will lose almost all mechanically occluded water. Some water of crystallization may remain, especially if sulfates are present. Organic matter may be lost by volatilization, but not completely destroyed. Loss of CO_2 results from conversion of bicarbonates to carbonates and carbonates may be decomposed partially to oxides or basic salts. Some chloride and nitrate salts may be lost. In general, evaporating and drying water samples at 180°C yields values for dissolved solids closer to those obtained through summation of individually determined mineral species than the dissolved solids values secured through drying at the lower temperature.

Results for residues high in oil or grease may be questionable because of the difficulty of drying to constant weight in a reasonable time.

Analyses performed for some special purposes may demand deviation from the stated procedures to include an unusual constituent with the measured solids. Whenever such variations of technique are introduced, record and present them with the results.

3. Sample Handling and Preservation

Use resistant-glass or plastic bottles, provided that the material in suspension does not adhere to container walls. Begin analysis as soon as possible because of the impracticality of preserving the sample. Refrigerate sample at 4°C up to analysis to minimize microbiological decomposition of solids.

4. Selection of Method

Methods A through E are suitable for the determination of solids in potable, surface, and saline waters, as well as domestic and industrial wastewaters in the range up to 20 000 mg/L.

Method F is suitable for the determination of solids in sediments, as well as solid and semisolid materials produced during water and wastewater treatment.

209 A. Total Solids Dried at 103-105°C

1. General Discussion

a. Principle: A well-mixed sample is evaporated in a weighed dish and dried to constant weight in an oven at 103 to 105°C. The increase in weight over that of the empty dish represents the total solids. The results may not represent the weight of

actual dissolved and suspended solids in wastewater samples (see above).

b. Interferences: Highly mineralized water with a significant concentration of calcium, magnesium, chloride, and/or sulfate may be hygroscopic and require prolonged drying, proper desiccation, and rapid weighing. Exclude large, floating particles or submerged agglomerates of nonhomogeneous materials from the sample if it is determined that their inclusion is not desired in the final result. Disperse visible floating oil and grease with a blender before withdrawing a sample portion for analysis. Because excessive residue in the dish may form a water-trapping crust, limit sample to no more than 200 mg residue.

2. Apparatus

a. Evaporating dishes: Dishes of 100-mL capacity made of one of the following materials:

1) Porcelain, 90-mm diam.

2) Platinum—Generally satisfactory for all purposes.

3) High-silica glass.*

b. Muffle furnace for operation at 550 ± 50°C.

c. Steam bath.

d. Desiccator, provided with a desiccant containing a color indicator of moisture concentration.

e. Drying oven, for operation at 103 to 105°C.

f. Analytical balance, capable of weighing to 0.1 mg.

3. Procedure

a. Preparation of evaporating dish: If volatile solids are to be measured ignite clean evaporating dish at 550 ± 50°C for 1 h in a muffle furnace. If only total solids are to be measured, heat clean dish to 103 to 105°C for 1 h. Store dish in desiccator until needed. Weigh immediately before use.

b. Sample analysis: Choose a sample volume that will yield a residue between 2.5 mg and 200 mg. Transfer a measured volume of well-mixed sample to preweighed dish and evaporate to dryness on a steam bath or in a drying oven. If necessary, add successive sample portions to the same dish after evaporation. When evaporating in a drying oven, lower temperature to approximately 2°C below boiling to prevent splattering. Dry evaporated sample for at least 1 h in an oven at 103 to 105°C, cool dish in desiccator to balance temperature, and weigh. Repeat cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained, or until weight loss is less than 4% of previous weight or 0.5 mg, whichever is less.

4. Calculation

$$\text{mg total solids/L} = \frac{(A - B) \times 1000}{\text{sample volume, mL}}$$

where:

A = weight of dried residue + dish, mg, and
B = weight of dish, mg.

5. Precision and Accuracy

Single-laboratory duplicate analyses of 41 samples of water and wastewater were made with a standard deviation of differences of 6.0 mg/L.

*Vycor, product of Corning Glass Works, Corning, N.Y., or equivalent.

der or reflocculation period and compression shoulder. Calculate interfacial settling rate as slope of line in centimeters per minute.

5. Precision and Accuracy

Accuracy is not applicable. The precision for this test has not been determined.

213 E. Specific Gravity

1. General Discussion

The specific gravity of a sludge is the ratio of the masses of equal volumes of a sludge and distilled water. It is determined by comparing the mass of a known volume of a homogeneous sludge sample at a specific temperature to the mass of the same volume of distilled water at 4°C.

2. Apparatus

Container: A marked flask or bottle to hold a known sludge volume during weighing.

3. Procedure

Follow either *a* or *b*.

a. Record sample temperature, *T*. Weigh empty container and record weight, *W*. Fill empty container to mark with sample, weigh, and record weight, *S*. Fill empty container to mark with water, weigh, and record weight, *R*. Measure all masses to the nearest 10 mg.

b. If sample does not flow readily, add as much of it to container as possible without exerting pressure, record volume, weigh, and record mass, *P*. Fill container to mark with distilled water, taking care that air bubbles are not trapped in the sludge or container. Weigh and record mass, *Q*. Measure all masses to nearest 10 mg.

4. Calculation

Use *a* or *b*, matching choice of procedure above.

TABLE 213:I. TEMPERATURE CORRECTION FACTOR

Temperature °C	Temperature Correction Factor
15	0.9991
20	0.9982
25	0.9975
30	0.9957
35	0.9941
40	0.9922
45	0.9903

a. Calculate specific gravity, *SG*, from the formula

$$SG_{T/4^\circ C} = \frac{\text{weight of sample}}{\text{weight of equal volume of water at 4°C}} = \frac{S - W}{R - W} \times F$$

The values of the temperature correction factor *F* are given in Table 213:I.

b. Calculate specific gravity, *SG*, from the formula

$$SG_{T/4^\circ C} = \frac{\text{weight of sample}}{\text{weight of equal volume of water at 4°C}} = \frac{(P - W)}{(R - W) - (Q - P)} \times F$$

For values of *F*, see Table 213:I.

METHOD 7470

MERCURY (MANUAL COLD-VAPOR TECHNIQUE)

1.0 Scope and Application

1.1 Method 7470 is a cold-vapor atomic absorption procedure approved for determining the concentration of mercury in mobility procedure extracts, aqueous wastes and groundwaters. (Method 7470 can also be used for analyzing certain solid and sludge-type wastes; however, Method 7471 is usually the method of choice for these waste types.) All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 Summary of Method

2.1 Prior to analysis, the samples must be prepared according to the procedure discussed in this method.

2.2 Method 7470, a cold-vapor atomic absorption technique, is based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.3 The typical detection limit for this method is 0.0002 mg/l.

3.0 Interferences

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/l of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from Type II water.

3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/l had no effect on recovery of mercury from spiked samples.

3.3 Seawaters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 ml) since, during the oxidation step, chlorides are converted to free chlorine which also absorbs radiation of 253 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 ml). In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater using this technique.

3.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer or equivalent: Any atomic absoption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

4.2 Mercury hollow cathode lamp or electrodeless discharge lamp.

4.3 Recorder: Any multirange variable speed recorder that is compatible with the UV detection system is suitable.

4.4 Absorption cell: Standard spectrophotometer cells 10 cm long having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing, 1 in. O.D. x 4.5 in. The ends are ground perpendicular to the longitudinal axis and quartz windows (1 in. diameter x 1/16 in. thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2-in. x 2-in. cards. One-in.-diameter holes are cut in the middle of each card. The cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

4.5 Air pump: Any peristaltic pump capable of delivering 1 liter air/min may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

4.6 Flowmeter: Capable of measuring an air flow of 1 liter/min.

4.7 Aeration tubing: A straight glass frit having a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

4.8 Drying tube: 6-in. x 3/4-in.-diameter tube containing 20 g of magnesium perchlorate or a small reading lamp with 60-W bulb which may be used to prevent condensation of moisture inside the cell. The lamp should be positioned to shine on the absorption cell so that the air temperature in the cell is about 10° C above ambient.

4.9 The cold-vapor generator is assembled as shown in Figure 1.

4.10 The apparatus shown in Figure 1 is a closed system. An open system, where the mercury vapor is passed through the absorption cell only once, may be used instead of the closed system.

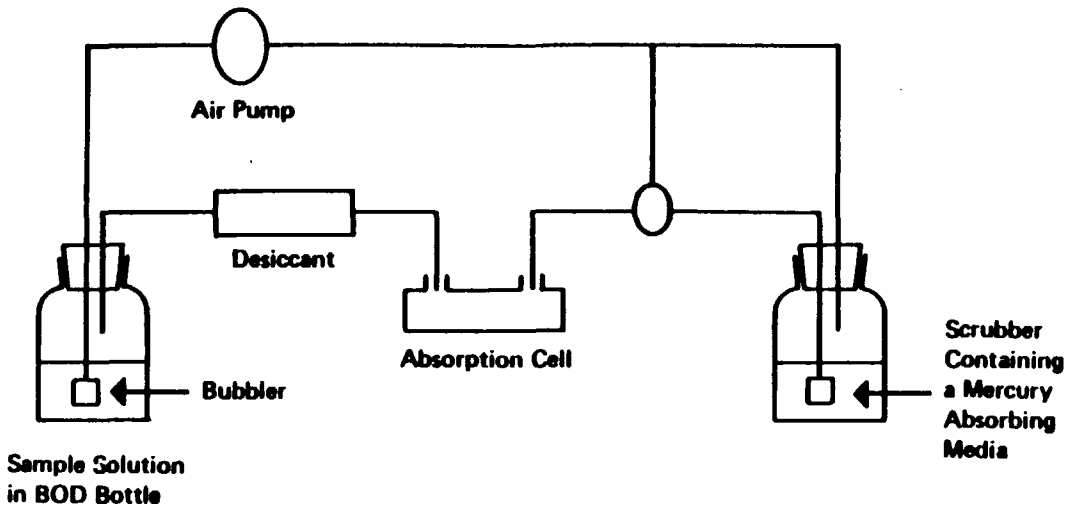

Figure 1. Apparatus for flameless mercury determination.

4.11 Because mercury vapor is toxic, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as:

1. equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4
2. 0.25% iodine in a 3% KI solution

A specially treated charcoal that will adsorb mercury vapor is also available from Barnebey and Cheney, E. 8th Ave. and N. Cassidy St., Columbus, Ohio 43219, Cat. #580-13 or #580-22.

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Sulfuric acid, conc.: Reagent grade.

5.3 Sulfuric acid, 0.5 N: Dilute 14.0 ml of conc. sulfuric acid to 1.0 liter.

5.4 Nitric acid, conc.: Reagent grade of low mercury content. If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

5.5 Stannous sulfate: Add 25 g stannous sulfate to 250 ml of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)

5.6 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in Type II water and dilute to 100 ml. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

5.7 Potassium permanganate, 5% solution (w/v): Dissolve 5 g of potassium permanganate in 100 ml of Type II water.

5.8 Potassium persulfate, 5% solution (w/v): Dissolve 5 g of potassium persulfate in 100 ml of Type II water.

5.9 Stock mercury solution: Dissolve 0.1354 g of mercuric chloride in 75 ml of Type II water. Add 10 ml of conc. HNO_3 and adjust the volume to 100.0 ml (2 ml = 1 mg Hg).

5.10 Mercury working standard: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 µg per ml. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before addition of the aliquot.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid. The suggested maximum holding times for these samples are 38 days in glass containers and 13 in plastic containers.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

7.0 Procedure

7.1 Sample preparation: Transfer 100 ml, or an aliquot diluted to 100 ml, containing not more than 1.0 µg of mercury, to a 300-ml BOD bottle. Add 5 ml of sulfuric acid and 2.5 ml of conc. nitric acid, mixing after each addition. Add 15 ml of potassium permanganate solution to each sample bottle. Sewage samples may require additional permanganate. Shake and add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 min. Add 8 ml of potassium persulfate to each bottle and heat for 2 hr in a water bath maintained at 95° C. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate. After a delay of at least 30 sec, add 5 ml of stannous sulfate and immediately attach the bottle to the aeration apparatus and continue as described in Section 7.3.

7.2 Standard preparation: Transfer 0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10.0-ml aliquots of the mercury working standard containing 0 to 1.0 µg of mercury to a series of 300-ml BOD bottles. Add enough Type II water to each bottle to make a total volume of 100 ml. Mix thoroughly and add 5 ml of conc. sulfuric acid and 2.5 ml of conc. nitric acid to each bottle. Add 15 ml of $KMnO_4$ solution to each bottle and allow to stand at least 15 min. Add 8 ml of potassium persulfate to each bottle and heat for 2 hr in a water bath maintained at 95° C. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. When the solution has been decolorized, wait 30 sec, add 5 ml of the stannous sulfate solution, and immediately attach the bottle to the aeration apparatus and continue as described in Section 7.3.

7.3 Analysis: At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter/min, is allowed to run continuously. The absorbance will increase and reach a maximum within 30 sec. As soon as the recorder pen levels off (approximately 1 min), open the bypass valve and continue the aeration until the absorbance returns to its minimum value. Close the bypass valve, remove the stopper and frit from the BOD bottle, and continue the aeration.

7.4 Construct a calibration curve by plotting the absorbance of standards versus micrograms of mercury. Determine the peak height of the unknown from the chart and read the mercury value from the standard curve.

7.5 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.6 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.7 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

MERCURY IN SOLID OR SEMISOLID WASTE (MANUAL COLD-VAPOR TECHNIQUE)

1.0 Scope and Application

1.1 Method 7471 is approved for measuring total mercury (organic and inorganic) in soils, sediments, bottom deposits, and sludge-type materials. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 Summary of Method

2.1 Prior to analysis the samples must be prepared according to the procedures discussed in this method.

2.2 Method 7471, a cold-vapor atomic absorption method, is based on the absorption of radiation at the 253.7-nm wavelength by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.3 The typical detection limit for this method is 0.0002 mg/l.

3.0 Interferences

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/l of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from Type II water.

3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/l had no effect on recovery of mercury from spiked samples.

3.3 Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 ml) since, during the oxidation step, chlorides are converted to free chlorine which also absorbs radiation of 253 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 ml). In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater using this technique.

3.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer or equivalent: Any atomic absoption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

4.2 Mercury hollow cathode lamp or electrodeless discharge lamp.

4.3 Recorder: Any multirange variable speed recorder that is compatible with the UV detection system is suitable.

4.4 Absorption cell: Standard spectrophotometer cells 10 cm long having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing, 1 in. O.D. x 4.5 in. The ends are ground perpendicular to the longitudinal axis and quartz windows (1 in. diameter x 1/16 in. thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2-in. x 2-in. cards. One-in.-diameter holes are cut in the middle of each card. The cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

4.5 Air pump: Any peristaltic pump capable of delivering 1 liter air/min may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

4.6 Flowmeter: Capable of measuring an air flow of 1 liter/min.

4.7 Aeration tubing: A straight glass frit having a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

4.8 Drying tube: 6-in. x 3/4-in.-diameter tube containing 20 g of magnesium perchlorate or a small reading lamp with 60-W bulb which may be used to prevent condensation of moisture inside the cell. The lamp should be positioned to shine on the absorption cell so that the air temperature in the cell is about 10° C above ambient.

4.9 The cold-vapor generator is assembled as shown in Figure 1.

4.10 The apparatus shown in Figure 1 is a closed system. An open system, where the mercury vapor is passed through the absorption cell only once, may be used instead of the closed system.

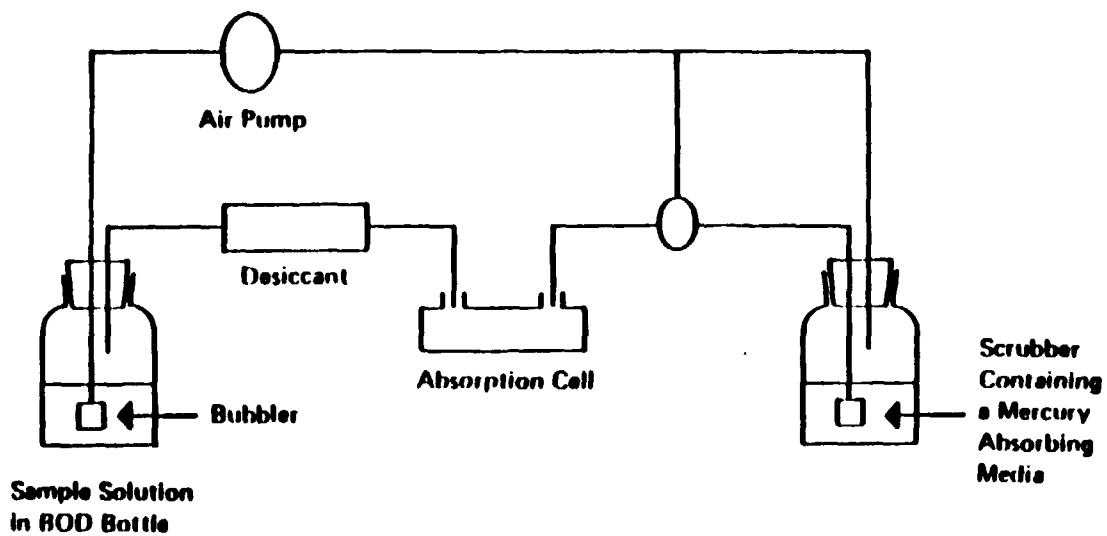

Figure 1. Apparatus for flameless mercury determination.

4.11 Because mercury vapor is toxic, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as:

3 4 00043

1. equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4
2. 0.25% iodine in a 3% KI solution

A specially treated charcoal that will adsorb mercury vapor is also available from Barnebey and Cheney, E. 8th Ave. and N. Cassidy St., Columbus, Ohio 43219, Cat. #580-13 or #580-22.

5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Aqua regia: Prepare immediately before use by carefully adding three volumes of conc. HCl to one volume of conc. HNO_3.

5.3 Sulfuric acid, 0.5 N: Dilute 14.0 ml of conc. sulfuric acid to 1 liter.

5.4 Stannous sulfate: Add 25 g stannous sulfate to 250 ml of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. A 10% solution of stannous chloride can be substituted for stannous sulfate.

5.5 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in Type II water and dilute to 100 ml. Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.

5.6 Potassium permanganate, 5% solution (w/v): Dissolve 5 g of potassium permanganate in 100 ml of Type II water.

5.7 Mercury stock solution: Dissolve 0.1354 g of mercuric chloride in 75 ml of distilled water. Add 10 ml of conc. nitric acid and adjust the volume to 100.0 ml (1.0 ml = 1.0 mg Hg).

5.8 Mercury working standard: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 µg/ml. This working standard and the dilution of the stock mercury solutions should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before adding the aliquot.

6.0 Sample Collection, Preservation, and Handling

3 4 00044

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 For solids or semi-solids, moisture may be driven off in a drying oven at a temperature of 60° C.

7.0 Procedure

7.1 Sample preparation: Weigh triplicate 0.2-g portions of dry sample and place in the bottom of a BOD bottle. Add 5 ml of Type II water and 5 ml of aqua regia. Heat 2 min in a water bath at 95° C. Cool, add 50 ml Type II water and 15 ml potassium permanganate solution to each sample bottle. Mix thoroughly and place in the water bath for 30 min at 95° C. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate. Add 55 ml of Type II water. Treating each bottle individually, add 5 ml of stannous sulfate and immediately attach the bottle to the aeration apparatus. Continue as described under 7.4.

7.2 An alternate digestion procedure employing an autoclave may also be used. In this method, 5 ml of conc. H_2SO_4 and 2 ml of conc. HNO_3 are added to the 0.2 g of sample. Add 5 ml of saturated $KMnO_4$ solution and cover the bottle with a piece of aluminum foil. The samples are autoclaved at 121° C and 15 lb for 15 min. Cool, dilute to a volume of 100 ml with Type II water and add 6 ml of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Purge the dead air space and continue as described under 7.4.

7.3 Standard preparation: Transfer 0.0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10-ml aliquots of the mercury working standard containing 0 to 1.0 µg of mercury to a series of 300-ml BOD bottles. Add enough Type II water to each bottle to make a total volume of 10 ml. Add 5 ml of aqua regia and heat 2 min in a water bath at 95° C. Allow the sample to cool and add 50 ml Type II water and 15 ml of $KMnO_4$ solution to each bottle and return to the water bath for 30 min. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Add 50 ml of Type II water. Treating each bottle individually, add 5 ml of stannous sulfate solution and immediately attach to bottle to the aeration apparatus and continue as described in Section 7.4.

7.4 Analysis: At this point, the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter/min, is allowed to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 sec. As soon as the recorder pen

levels off (approximately 1 min), open the bypass valve and continue the aeration until the absorbance returns to its minimum value. Close the bypass value, remove the fritted tubing from the BOD bottle, and continue the aeration.

7.5 Construct a calibration curve by plotting the absorbance of standards versus micrograms of mercury. Determine the peak height of the unknown from the chart and read the mercury value from the standard curve.

7.6 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.7 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.8 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

METHOD 8250

GC/MS METHOD FOR SEMIVOLATILE ORGANICS:
PACKED COLUMN TECHNIQUE

1.0 Scope and Application

1.1 Method 8250 is used to determine the concentration of semivolatile organic compounds (see Tables 1 and 2) in a variety of solid waste matrices.

1.2 This method is applicable to nearly all types of samples, regardless of water content, including groundwater, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments.

1.3 Method 8250 can be used to quantify most neutral, acidic, and basic organic compunds that are soluble in methylene chloride and capable of being eluted without derivatization as sharp peaks from a gas chromatographic column. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols.

1.4 The detection limit of Method 8250 for determining an individual compound is approximately 1 µg/g (wet weight) in waste samples. For samples that contain more than 1 mg/g of total solvent extractable material, the detection limit is proportionately higher.

1.5 Method 8250 is based upon a solvent extraction, gas chromatographic/mass spectrometric (GC/MS) procedure.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 Summary of Method

2.1 Prior to using this method, the waste samples should be prepared for chromatography (if necessary) using the appropriate sample preparation method - i.e., separatory funnel liquid-liquid extraction (Method 3510), acid base extraction (Method 3530), sonication (Method 3550), or soxhlet extraction (Method 3540). For groundwater samples Method 3530 should be used. If emulsions are a problem, continuous extraction techniques should be used. This method describes chromatographic conditions which allow for the separation of the compounds in the extract.

TABLE 1. CHROMATOGRAPHIC CONDITIONS, METHOD DETECTION LIMITS, AND CHARACTERISTIC IONS FOR BASE/NEUTRAL EXTRACTABLES

Parameter	Retention time (min)	Method detection limit (µg/l)	Characteristic ions					
			Electron impact			Chemical ionization (methane)		
			Primary	Secondary				
1,3-Dichlorobenzene	7.4	1.9	146	148	113	146	148	150
1,4-Dichlorobenzene	7.8	4.4	146	148	113	146	148	150
Hexachloroethane	8.4	1.6	117	201	199	199	201	203
Bis(2-chloroethyl) ether	8.4	5.7	93	63	95	63	107	109
1,2-Dichlorobenzene	8.4	1.9	146	148	113	146	148	150
Bis(2-chloroisopropyl) ether	9.3	5.7	45	77	79	77	135	137
N-Nitrosodi-n-propyl amine			130	42	101			
Nitrobenzene	11.1	1.9	77	123	65	124	152	164
Hexachlorobutadiene	11.4	0.9	225	223	227	223	225	227
1,2,4-Trichlorobenzene	11.6	1.9	180	182	145	181	183	209
Isophorone	11.9	2.2	82	95	138	139	167	178
Naphthalene	12.1	1.6	128	129	127	129	157	169
Bis(2-chloroethoxy) methane	12.2	5.3	93	95	123	65	107	137
Hexachlorocyclopentadiene	13.9		237	235	272	235	237	239
2-Chloronaphthalene	15.9	1.9	162	164	127	163	191	203
Acenaphthylene	17.4	3.5	152	151	153	152	153	181
Acenaphthene	17.8	1.9	154	153	152	154	155	183
Dimethyl phthalate	18.3	1.6	163	194	164	151	163	164
2,6-Dinitrotoluene	18.7	1.9	165	89	121	183	211	223
Fluorene	19.5	1.9	166	165	167	166	167	195
4-Chlorophenyl phenyl ether	19.5	4.2	204	206	141			
2,4-Dinitrotoluene	19.8	5.7	165	63	182	183	211	223
Diethylphthalate	20.1	22	149	177	150	177	223	251
N-Nitrosodiphenylamine	20.5	1.9	169	168	167	169	170	198
Hexachlorobenzene	21.0	1.9	284	142	249	284	286	288
α-BHC	21.1		183	181	109			
4-Bromophenyl phenyl ether	21.2	1.9	248	250	141	249	251	277
γ-BHC	22.4		183	181	109			

TABLE 1. (CONT.)

Parameter	Retention time (min)	Method detection limit (µg/l)	Characteristic ions: Electron impact: Primary	Electron impact: Secondary		Chemical ionization (methane)		
Phenanthrene	22.8	5.4	178	179	176	178	179	207
Anthracene	22.8	1.9	178	179	176	178	179	207
β-BHC	23.4	4.2	181	183	109			
Heptachlor	23.4	1.9	100	272	274			
δ-BHC	23.7	3.1	183	109	181			
Aldrin	24.0	1.9	66	263	220			
Dibutyl phthalate	24.7	2.5	149	150	104	149	205	279
Heptachlor epoxide	25.6	2.2	353	355	351			
Endosulfan I	26.4	--	237	339	341			
Fluoranthene	26.5	2.2	202	101	100	203	231	243
Dieldrin	27.2	2.5	79	263	279			
4,4'-DDE	27.2	5.6	246	248	176			
Pyrene	27.3	1.9	202	101	100	203	231	243
Endrin	27.9	--	81	263	82			
Endosulfan II	28.6	--	237	339	341			
4,4'-DDD	28.6	2.8	235	237	165			
Benzidine	28.8	44	184	92	185	185	213	225
4,4'-DDT	29.3	4.7	235	237	165			
Endosulfan sulfate	29.8	5.6	272	387	422			
Endrin aldehyde	--	--	67	345	250			
Butyl benzyl phthalate	29.9	2.5	149	91	206	149	299	327
Bis(2-ethylhexyl) phthalate	30.6	2.5	149	167	279	149		
Chrysene	31.5	2.5	228	226	229	228	229	257
Benzo(a)anthracene	31.5	7.8	228	229	226	228	229	257
3,3'-Dichlorobenzidine	32.2	16.5	252	254	126			
Di-n-octyl phthalate	32.5	2.5	149					
Benzo(b)fluoranthene	34.9	4.8	252	253	125	252	253	281
Benzo(k)fluoranthene	34.9	2.5	252	253	125	252	253	281
Benzo(a)pyrene	36.4	2.5	252	253	125	252	253	281

TABLE 1. (CONT.)

Parameter	Retention time (min)	Method detection limit (µg/l)	Characteristic ions: Electron impact Primary	Electron impact Secondary		Chemical ionization (methane)		
Indeno(1,2,3-c,d)pyrene	42.7	3.7	276	138	277	276	277	305
Dibenzo(a,h)anthracene	43.2	2.5	278	139	279	278	279	307
Benzo(ghi)perylene	45.1	4.1	276	138	277	276	277	305
N-Nitrosodimethyl amine	--	--	42	74	44			
Chlordane[a]	19 to 30	--	373	375	377			
Toxaphene[a]	25 to 34	--	159	231	233			
PCB 1016[a]	18 to 30	--	224	260	294			
PCB 1221[a]	15 to 30	30	190	224	260			
PCB 1232[a]	15 to 32	--	190	224	260			
PCB 1242[a]	15 to 32	--	224	260	294			
PCB 1248[a]	12 to 34	--	294	330	362			
PCB 1254[a]	22 to 34	36	294	330	362			
PCB 1260[a]	23 to 32	--	330	362	394			

[a]These compounds are mixtures of various isomers (See Figures 2 to 12).

Gas chromatographic conditions: Glass column 1.8 m long x 2 mm I.D. packed with Supelcoport (100/120) coated with 3% SP-2250. Carrier gas: helium at a flow rate of 30 ml/min. Temperature: Isothermal at 50° C for 4 min, then 8° per min to 270° C. Hold at 270° C for 30 min.

TABLE 2. CHROMATOGRAPHIC CONDITIONS, METHOD DETECTION LIMITS, AND CHARACTERISTIC IONS FOR ACID EXTRACTABLES

Parameter	Retention time (min)	Method detection limit (µg/l)	Characteristic ions					
			Electron impact			Chemical ionization (methane)		
			Primary	Secondary				
2-Chlorophenol	5.9	3.3	128	64	130	129	131	157
2-Nitrophenol	6.5	3.6	139	65	109	140	168	122
Phenol	8.0	1.5	94	65	66	95	123	135
2,4-Dimethylphenol	9.4	2.7	122	107	121	123	151	163
2,4-Dichlorophenol	9.8	2.7	162	164	98	163	165	167
2,4,6-Trichlorophenol	11.8	2.7	196	198	200	197	199	201
4-Chloro-3-methylphenol	13.2	3.0	142	107	144	143	171	183
2,4-Dinotrophenol	15.9	42	184	63	154	185	213	225
2-Methyl-4,6-dinitrophenol	16.2	24	198	182	77	199	227	239
Pentachlorophenol	17.5	3.6	266	264	268	267	265	269
4-Nitrophenol	20.3	2.4	65	139	109	140	168	122

Chromatographic conditions: Glass column 1.8 m long x 2 mm I.D. packed with Supelcoport (100/120) coated with 1% SP-1240 DA. Carrier gas: helium at a flow rate of 30 ml/min. Column temperature, isothermal at 70° C for 2 min, then 8° per min to 200° C.

3.0 Interferences

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of chromatograms. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or waste being sampled.

3.2.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Heating in a muffle furnace at 450° C for 5 to 15 hr is recommended whenever feasible. Alternatively, detergent washes, water rinses, acetone rinses, and oven drying may be used. Cleaned glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants.

3.2.2 The use of high purity reagents and solvents helps to minimize interference problems.

4.0 Apparatus

4.1 Sampling equipment: Glass screw-cap vials or jars of at least 100-ml capacity. Screw caps must be Teflon lined.

4.2 Glassware

4.2.1 Beaker: 400-ml.

4.2.2 Centrifuge tubes: approximately 200-ml capacity, glass with screw cap (Corning #1261 or equivalent). Screw caps must be fitted with Teflon liners.

4.2.3 Concentrator tube, Kuderna-Danish: 25-ml, graduated (Kontes K 570050-2526 or equivalent). Calibration must be checked at the volumes employed in the test. Ground-glass stopper is used to prevent evaporation of extracts.

4.2.4 Evaporative flask: Kuderna-Danish 250-ml (Kontes K-570001-0250 or equivalent). Attach to concentrator tube with springs.

4.2.5 Snyder column, Kuderna-Danish: Three-ball macro (Kontes K-503000-0121 or equivalent).

4.2.6 Snyder column, Kuderna-Danish: Two-ball micro (Kontes K-569001-0219 or equivalent).

4.3 Filter assembly

4.3.1 Syringe: 10-ml gas-tight with Teflon Luerlock (Hamilton 1010TLL or equivalent).

4.3.2 Filter holder: 13-mm Swinny (Millipore XX30-012 or equivalent)

4.3.3 Prefilters: glass fiber (Millipore AP-20-010 or equivalent).

4.3.4 Membrane filter: 0.2-µm Teflon (Millipore FGLP-013 or equivalent)

4.4 Micro syringe: 100-µl (Hamilton #84858 or equivalent).

4.5 Weighing pans, micro: approximately 1-cm diameter aluminum foil. Purchase or fabricate from aluminum foil.

4.6 Boiling chips: Approximately 10-40 mesh carborundum (A.H. Thomas #1590-D30 or equivalent). Heat to 450° C for 5-10 hr or extract with methylene chloride.

4.7 Water bath: Heated, capable of temperature control (±2° C). The bath should be used in a hood.

4.8 Balance: Analytical, capable of accurately weighing 0.0001 g.

4.9 Microbalance: Capable of accurately weighing to 0.001 mg (Mettler model ME-30 or equivalent).

4.10 Homogenizer, high speed: Brinkmann Polytron model PT 10ST with Teflon bearings, or equivalent.

4.11 Centrifuge: Capable of accommodating 200-ml glass centrifuge tubes.

4.12 pH Meter and electrodes: Capable of accurately measuring pH to ±0.1 pH unit.

4.13 Spatula: Having a metal blade 1-2 cm in width.

4.14 Heat lamp: 250-watt reflector-type bulb (GE #250R-40/4 or equivalent) in a heat-resistant fixture whose height above the sample may be conveniently adjusted.

4.15 Gas chromatograph/mass spectrometer data system

4.15.1 Gas chromatograph: An analytical system complete with a temperature-programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases.

4.15.2 Column for base-neutral compounds: 2-m x 2-mm I.D. stainless steel or glass, packed with 3% SP-2250-DB on 100/120 mesh Supelcoport B or equivalent.

4.15.3 Column for acidic compounds: 2-m x 2-mm I.D. glass packed with 1% SP 1240-DA on 100/120 mesh Supelcoport.

4.15.4 Mass spectrometer: Capable of scanning from 35 to 450 amu every 3 sec or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all the criteria in Table 3 when 50 ng of decafluorotriphenylphosphine (DFTPP) is injected through the GC inlet.

TABLE 3. DFTPP KEY IONS AND ION ABUNDANCE CRITERIA[a]

Mass	Ion abundance criteria
51	30-60% of mass 198
68	Less than 2% of mass 69
70	Less than 2% of mass 69
127	40-60% of mass 198
197	Less than 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	Greater than 1% of mass 198
441	Present but less than mass 443
442	Greater than 40% of mass 198
443	17-23% of mass 442

[a]J.W. Eichelberger, L.E. Harris, and W.L. Budde. 1975. Reference compound to calibrate ion abundance measurement in gas chromatography-mass spectrometry. Analytical Chemistry 47:995.

4.15.4 GC/MS interface: Any GC-to-MS interface that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria (see Sections 7.2.1-7.2.4) may be used. GC-to-MS interfaces constructed of all glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane. The interface must be capable of transporting at least 10 ng of the components of interest from the GC to the MS.

4.15.5 Data system: A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits.

4.16 Gel permeation chromatography system

4.16.1 Chromatographic column: 600-mm x 25-mm I.D. glass column fitted for upward flow operation.

4.16.2 Bio-beads S-X8: 80 g per column.

4.16.3 Pump: Capable of constant flow of 0.1 to 5 ml/min at up to 100 psi.

4.16.4 Injector: With 5-ml loop.

4.16.5 Ultraviolet detector: 254 mm.

4.16.6 Strip chart recorder.

5.0 Reagents

5.1 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit of each compound of interest.

5.2 Potassium phosphate, tribasic (K_3PO_4): Granular (ACS).

5.3 Phosphoric acid (H_3PO_4): 85% aqueous solution (ACS).

5.4 Sodium sulfate, anhydrous (Na_2SO_4): Powder (ACS).

5.5 Methylene chloride: Distilled-in-glass quality (Burdick and Jackson, or equivalent).

5.6 D_{10}-Phenanthrene.

5.7 Decafluorotriphenylphosphine (DFTPP).

5.8 Retention time standards: D_3-Phenol, D_8-naphthalene, D_{10}-Phenanthrene, D_{12}-chrysene, and D_{12}-benzo(a)pyrene. D_{12}-perylene may be used in place of D_{12}-benzo(a)pyrene.

5.9 Column performance standards: D_3-phenol, D_5-aniline, D_5-nitrobenzene, and D_3-2,4-dinitrophenol.

5.10 Surrogate standards: Decafluorobiphenyl, 2-fluoroaniline, and pentafluorophenol.

5.11 GPC calibration solution: Methylene chloride containing 100 mg corn oil, 20 mg di-n-octyl phthalate, 3 mg coronene, and 2 mg sulfur per 100 ml.

6.0 Sample Collection, Preservation, and Handling

6.1 Grab samples must be collected in glass containers having Teflon-lined screw caps. Sampling equipment must be free of oil and other potential sources of contamination.

6.2 The samples must be iced or refrigerated at 4° C from the time of collection until extraction.

6.3 All samples must be extracted within 14 days of collection and completely analyzed within 40 days of extraction.

7.0 Procedure

7.1 Calibration

7.1.1 An internal standard calibration procedure is used. To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that measurement of the internal standard is not affected by method or matrix interferences. D_{10}-phenanthrene is recommended for this purpose for general use. Use the base peak ion as the primary ion for quantification of the standards. If interferences are noted, use the next most intense ion as the secondary ion. The internal standard is added to all calibration standards and all sample extracts analyzed by GC/MS. Retention time standards, column performance standards, and a mass spectrometer tuning standard are included in the internal standard solution used.

7.1.1.1 A set of five or more retention time standards is selected that will permit all components of interest in a chromatogram to have retention times of 0.85 to 1.20 relative to at least one of the retention time standards. The retention time standards should be similar in analytical behavior to the compounds of interest and their measurement should not be affected by method or matrix interferences. The following retention time standards are recommended for general use: D_3-phenol, D_8-naphthalene, D_{12}-chrysene, and D_{12}-benzo(a)pyrene. D_{15}-perylene may be substituted for D_{12}-benzo(a)pyrene. D_{10}-phenanthrene serves as a retention time standard as well as an internal standard.

7.1.1.2 Representative acidic, basic, and polar netural compounds are added with the internal standard to assess the column performance of the GC/MS system. The measurement of the column performance standards should not be affected by method or matrix interferences. The following column performance standards are recommended for general use: D_5-phenol, D_5-aniline, D_5-nitrobenzene, and D_3-2,4-dinitrophenol. These compounds can also serve as retention time standards if appropriate and the retention time standards recommended in Section 7.1.1.1 can serve as column performance standards if appropriate.

7.1.1.3 Decafluorotriphenylphosphine (DFTPP) is added to the internal standard solution to permit the mass spectrometer tuning for each GC/MS run to be checked.

7.1.1.4 Prepare the internal standard solution by dissolving, in 50.0 ml of methylene chloride, 10.0 mg of each standard compound specified in Sections 7.1.1.1, 7.1.1.2, and 7.1.1.3. The resulting solution will contain each standard at a concentration of 200 µg/ml.

7.1.2 Prepare calibration standards at a minimum of three concentration levels for each compound of interest. Each ml of each calibration standard or standard mixture should be mixed with 250 µl of the internal standard solution. One of the calibration standards should be at a concentration near, but above, the method detection limit, 1 to 10 µg/ml, and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC/MS system.

7.1.3 Analyze 1 µl of each calibration standard and tabulate the area of the primary characteristic ion against concentration for each compound including standard compound. Calculate response factors (RF) for each compound as follows:

$$RF = (A_s C_{is})/(A_{is} C_s)$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standards.

C_{is} = Concentration of the internal standard in µg/l.

C_s = Concentration of the compound to be measured in µg/l.

If the RF value over the working range is constant (less than 20% relative standard deviation), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is}, against RF.

7.1.4 The RF must be verified on each working day by the measurement of two or more calibration standards, including one at the beginning of the day and one at the end of the day. The response factors obtained for the calibration standards analyzed immediately before and after a set of samples must be within ±20% of the response factor used for quantification of the sample concentrations.

7.2 Daily GC/MS performance tests

7.2.1 At the beginning of each day that analyses are to be performed, the GC/MS system must be checked to see that acceptable performance criteria are achieved for DFTPP.

7.2.2 The DFTPP performance test requires the following instrumental parameters:

Electron energy: 70 volts (nominal)

Mass Range: 40 to 450 amu

Scan Time: 1 sec per scan

7.2.3 Inject a solution containing 50 µg/ml of DFTPP into the GC/MS system or bleed DFTPP vapor directly into the mass spectrometer and tune the instrument to achieve all the key ion criteria for the mass spectrum of DFTPP given in Table 1.

7.2.4 DFTPP is included in the internal standard solution added to all samples and calibration solutions. If any key ion abundance observed for DFTPP during the analysis of a sample differs by more than 10% from that observed during the analysis of the calibration solution, then the analysis in question is considered invalid. The instrument

must be retuned or the sample and/or calibration solution reanalyzed until the above condition is met.

7.3 Sample extraction

7.3.1 The extraction procedure involves homogenization of the sample with methylene chloride, neutralization to pH 7, and the addition of anhydrous sodium sulfate to remove the water. The amount of acid or base required for the neutralization is determined by titration of the sample. Aqueous samples are extracted using Method 3510 while organic liquids may be analyzed neat or diluted with CH_2 and analyzed. Solids and semisolids are extracted by Method 3540 and 3550 or by the extraction described in Steps 7.3.1 through 7.4.3.

7.3.1.1 Thoroughly mix the sample to enable a representative sample to be obtained. Weight 3.0 g (wet weight) of sample into a 400-ml beaker. Add 75 ml methylene chloride and 150 ml water.

7.3.1.2 Homogenize the mixture for a total of 1 min using a high-speed homogenizer. Use a metal spatula to dislodge any material that adheres to the beaker or to the homogenizer before or during the homogenization to ensure thorough dispersion of the sample.

7.3.1.3 Adjust the pH of the mixture to 7.0 $\pm$ 0.2 by titration with 0.4 M H_3PO_4 or 0.4 M K_3PO_4 using a pH meter to measure the pH. Record the volume of acid or base required.

7.3.2 The extraction with methylene chloride is performed using a fresh portion of the sample. Weigh 3.0 g (wet weight) of sample into a 200-ml centrifuge tube. Spike the sample with surrogate standards as described in Section 8.4. Add 150 ml of methylene chloride followed by 1.0 ml of 4 M phosphate buffer pH 7.0, and an amount of 4 M H_3PO_4 or 4 M K_3PO_4 equal to one tenth of the pH 7 acid or base volume requirement determined in Section 7.3.1.3. For example, if the acid requirement in Section 7.3.1.3 was 2.0 ml of 0.4 M H_3PO_4, the amount of 4 M H_3PO_4 needed would be 0.2 ml.

7.3.3 Homogenize the mixture for a total of 30 sec using a high-speed homogenizer at full speed. Cool the mixture in an ice bath or cold water bath, if necessary, to maintain a temperature of 20-30° C. Use a metal spatula to help dislodge any material that adheres to the centrifuge tube or homogenizer during the homogenization to obtain as thorough a dispersion of the sample as possible. Some samples, especially those that contain much water, may not disperse well in this step but will disperse after sodium sulfate is added. Add an amount of anhydrous sodium sulfate powder equal to 15.0 g plus 3.0 g per ml of the 4 M H_3PO_4 or 4 M K_3PO_4 added in Section 7.3.2. Homogenize the mixture again for a total of 30 sec using a high-speed homogenizer at full speed. Use a metal spatula to dislodge any material that adheres to the centrifuge tube or homogenizer during the homogenization to ensure thorough dispersion. (NOTE: This step may cause rapid deterioration of the Teflon bearing in the homogenizer. The bearing

must be replaced whenever the rotor shaft becomes loose to prevent damage to stainless steel parts.) Allow the mixture to stand until a clear supernatant is obtained. Centrifuge if necessary to facilitate the phase separation. Filter the supernatant required for Sections 7.3.4, 7.3.5, and 7.3.7 (at least 2 ml) through a 0.2-μm Teflon filter.

7.3.4 Estimate the total solvent extractable content (TSEC) of the sample by determining the residue weight of an aliquot of the supernatant from Section 7.3.3. Transfer 0.1 ml of the supernatant to a tared aluminum weighing dish, place the weighing dish under a heat lamp at a distance of 8 cm from the lamp for 1 min to allow the solvent to evaporate, and weigh on a microbalance. If the residue weight of the 0.1-ml aliquot is less than 0.05 mg, concentrate 25 ml of the supernatant to 1.0 ml and obtain a residue weight on 0.1 ml of the concentrate. For the concentration step, use a 25-ml evaporator tube fitted with a micro Snyder column; add two boiling chips and heat in a water bath at 60-65° C. Calculate the TSEC as milligrams of residue per gram of sample using Equation 1 if concentration was not required or Equation 2 if concentration was required.

$$\frac{\text{mg of residue}}{\text{g of sample}} = \frac{\text{residue weight (mg) of 0.1 ml of supernatant}}{0.002} \qquad \text{(Eq. 1)}$$

$$\frac{\text{mg of residue}}{\text{g of sample}} = \frac{\text{residue weight (mg) of 0.1 ml of conc. supernatant}}{0.05} \qquad \text{(Eq. 2)}$$

7.3.5 If the TSEC of the sample (as determined in Section 7.3) is less than 50 mg/g, concentrate an aliquot of the supernatant that contains a total of only 10 to 20 mg of residual material. For example, if the TSEC is 44 mg/g, use a 20-ml aliquot of the supernatant, which will contain 17.6 mg of residual material, or if the TSEC is 16 mg/g, use a 50-ml aliquot of the supernatant, which will contain 16.0 mg of residual material. If the TSEC is less than 10 mg/g, use 100 ml of the supernatant. Perform the concentration by transferring the aliquot of the supernatant to a K-D flask fitted into a 25-ml concentrator tube. Add two boiling chips, attach a three-ball macro Snyder column to the K-D flask, and concentrate the extract using a water bath at 60 to 65° C. Place the K-D apparatus in the water bath so that the concentrator tube is about half immersed in the water and the entire rounded surface of the flask is bathed with water vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 min. At the proper rate of distillation, the balls of the column actively chatter but the chambers do not flood. When the liquid has reached an apparent volume of 5 to 6 ml, remove the K-D apparatus from the water bath and allow the solvent to drain for at least 5 min while cooling. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with the methylene chloride to bring the volume to 10.0 ml. Mix the contents of the concentrator tube by inserting a stopper and inverting several times.

7.3.6 Analyze the concentrate from Section 7.3.5 or, if the TSEC of the sample is 50 mg/g or more, analyze the supernatant from Section 7.3 using gas chromatography. Use a 30-m x 0.25-mm bonded-phase silicone-coated fused-silica capillary column under the chromatographic conditions described in Section 7.5. Estimate the concentration factor or dilution factor required to give the optimum concentration for the subsequent GC/MS analysis. In general, the optimum concentration will be one in which the average peak height of the five largest peaks or the height of an unresolved envelope of peaks is the same as that of an internal standard at a concentration of 50-100 µg/ml.

7.3.7 If the optimum concentration determined in Section 7.3.6 is 20 mg of residual material per ml or less, proceed to Section 7.3.8. If the optimum concentration is greater than 20 mg of residual material per ml and if the TSEC is greater than 50 mg/g, apply the GPC cleanup procedure described in Section 7.4. For the GPC cleanup, concentrate 90 ml of the supernatant from Section 7.3.3 or a portion of the supernatant that contains a total of 600 mg of residual material (whichever is the smaller volume). Use the concentration procedure described in Section 7.3.5 and concentrate to a final volume of 15.0 ml. Stop the concentration prior to reaching 15.0 ml if any oily or semisolid material separates out and dilute as necessary (up to a maximum final volume equal to the volume of supernatant used) to redissolve the material. (Disregard the presence of small amounts of inorganic salts that may settle out.)

7.3.8 Concentrate further or dilute as necessary an aliquot of the concentrate from Section 7.3.5 or an aliquot of the supernatant from Section 7.3.3, or if GPC cleanup was necessary, an aliquot of the concentrate from Section 7.4.3 to obtain 1.0 ml of a solution having the optimum concentration, as described in Section 7.3.6, for the GC/MS analysis. If the aliquot needs to be diluted, dilute it to a volume of 1.0 ml with methylene chloride. If the aliquot needs to be concentrated, concentrate it to 1.0 ml as decribed in Section 7.3.4. Do not let the volume in the concentrator tube go below 0.6 ml at any time. Stop the concentration prior to reaching 1.0 ml if any oily or semisolid material separates out and dilute as necessary (up to a maximum final volume of 10 ml) to redissolve the material. (Disregard the presence of small amounts of inorganic salts that may settle out). Add 250 µl of the internal standard solution, containing 50 µg each of the internal standard, retention time standards, column performance standards, and DFTPP, to 1.0 ml of the final concentrate and save for GC/MS analysis as described in Section 7.5. Calculate the concentration in the original sample that is represented by the internal standard using Equation 3 if an aliquot of the concentrate from Section 7.3.5 was used in Section 7.3.8, Equation 4 if an aliquot of the supernatant from Section 7.3.3 was used in Section 7.3.8 or Equation 5 if an aliquot of the GPC concentrate from Section 7.4.3 was used in Section 7.3.8.

$$\frac{\mu g \text{ of Int. Std.}}{g \text{ of sample}} = \frac{50}{3} \times \frac{150}{V_{s(7.3.5)}} \times \frac{10}{V_{c\ (7.3.8)}} \times \frac{\text{Final Vol. (ml)}}{1} \quad \text{(Eq. 3)}$$

$$\frac{\mu g \text{ of Int. Std.}}{g \text{ of sample}} = \frac{50}{3} \times \frac{150}{V_{s(7.3.8)}} \times \frac{\text{Final Vol. (ml)}}{1} \quad \text{(Eq. 4)}$$

$$\frac{\mu g \text{ of Int. Std.}}{g \text{ of sample}} = \frac{50}{3} \times \frac{150}{V_{s(7.3.7)}} \times \frac{V_F}{V_{GPC\ (7.3.7)}} \times \frac{\text{Final Vol. (ml)}}{1} \quad \text{(Eq. 5)}$$

where:

V_S = Volume of supernatant from Section 7.3.3 used in Sections 7.3.5, 7.3.8, 7.3.7

$V_{C(7.3.8)}$ = Volume of concentrate from Section 7.3.5 used in Section 7.3.8

$V_{F\ (7.3.7)}$ = Final volume of concentrate in Section 7.3.7

V_{GPC} = Volume of GPC concentrate from Section 7.4.3 used in Section 7.3.8

Use this calculated value for the quantification of individual compounds as described in Section 7.7.2.

7.4 Cleanup using gel permeation chromatography

7.4.1 Prepare a 600-mm x 25-mm I.D. gel permeation chromatography (GPC) column by slurry packing using 80 g of Bio-Beads S-X8 that have been swelled in methylene chloride for at least 4 hr. Prior to initial use, rinse the column with methylene chloride at 1 ml/min for 16 hr to remove any traces of contaminants. Calibrate the system by injecting 5 ml of the GPC calibration solution, eluting with methylene chloride at 5 ml/min for 50 min and observing the resultant UV detector trace. The column may be used indefinitely as long as no darkening or pressure increases occur and a column efficiency of at least 500 theoretical plates is achieved. The pressure should not be permitted to exceed 50 psi. Recalibrate the system daily.

7.4.2 Inject a 5-ml aliquot of the concentrate from Section 7.3.7 onto the GPC column and elute with methylene chloride at 5 ml/min for 50 min. Discard the first fraction that elutes up to a retention time represented by the minimum between the corn oil peak and the di-n-octyl phthalate peak in the calibration run. Collect the next fraction eluting up to a retention time represented by the minimum between the coronene peak and the sulfur peak in the calibration run. Apply the

above GPC separation to a second 5-ml aliquot of the concentrate from Section 7.3.7 and combine the fractions collected.

7.4.3 Concentrate the combined GPC fractions to 10.0 ml as described in Section 7.3.5. Estimate the TSEC of the concentrate as described in Section 7.3.4. Estimate the TSVC of the concentrate as described in Section 7.3.6.

7.5 Gas chromatography/mass spectrometry

7.5.1 Analyze the 1-ml concentrate from Method 3510, 3540, or 3550, or Section 7.3.8 by GC/MS using the appropriate column (see Section 4.15). The recommended GC operating conditions to be used are as follows:

Conditions for base neutral analysis (3% SP-2250-DB)

Initial column temperature hold: 50° C for 4 min

Column temperature program: 50-300° C at 8 degrees/min

Final column temperature hold: 300° C for 20 min.

Conditions for acid analysis (1% SP-1240-DA)

Initial column temperature: 70° C for 2 min

Column temperature program: 70-200° C at 8 degrees/min

Final column temperature hold: 200° C for 20 min

Injector temperature: 300° C

Transfer line temperature: 300° C

Sample volume: 1-2 µl

Carrier gas: Helium at 30 ml/min

7.5.2 If the response for any ion exceeds the working range of the GC/MS system, dilute the extract and reanalyze.

7.5.3 Perform all qualitative and quantitative measurements as described in Sections 7.6 and 7.7. When the extracts are not being used for analyses, store them at 4° C protected from light in screw-cap vials equipped with unpierced Teflon-lined septa.

7.6 Qualitative identification. Obtain an EICP for the primary characteristic ion and at least two other characteristic ions for each compound when practical. The following criteria must be met to make a qualitative identification.

7.6.1 The characteristic ions for each compound of interest must maximize in the same or within one scan of each other.

7.6.2 The retention time must fall within ± 15 sec (based on the relative retention time) of the retention time of the authentic compound.

7.6.3 The relative peak heights of the characteristic ions in the EICP's must fall within ±20% of the relative intensities of these ions in a reference mass spectrum.

7.7 Quantitative determination

7.7.1 When a compound has been identified, the quantification of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. In general, the primary characteristic ion selected should be a relatively intense ion as interference-free as possible, and as close as possible in mass to the characteristic ion of the internal standard used.

7.7.2 Use the internal standard technique for performing the quantification. Calculate the concentration of each individual compound of interest in the sample using Equation 6.

$$\text{Concentration, } \mu g/g = \frac{\mu g \text{ of Int. Std.}}{g \text{ of sample}} \times \frac{A_s}{A_{is}} \times \frac{1}{RF} \qquad \text{(Eq. 6)}$$

where:

$\frac{\mu g \text{ of Int. Std.}}{g \text{ of sample}}$ = internal standard concentration factor calculated in Section 7.3.8

A_s = Area of the primary characteristic ion of the compound being quantified

A_{is} = Area of the primary characteristic ion of the internal standard

RF = Response factor of the compound being quantified (determined in Section 7.1.3).

7.7.3 Report results in µg/g without correction for recovery data. When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

7.7.4 If the surrogate standard recovery falls outside the control limits in Section 8.3, the data for all compounds in that sample must be labeled as suspect.

8.0 Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data that is generated. Ongoing performance checks must be compared with established performance criteria to determine if the results of analyses are within the accuracy and precision limits expected of the method.

8.1.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 The laboratory must spike all samples including check samples with surrogate standards to monitor continuing laboratory performance. This procedure is described in Section 8.4.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations using a representative sample as a check sample.

8.2.1 Analyze four aliquots of the unspiked check sample according to the method beginning in Section 7.3.

8.2.2 For each compound to be measured, select a spike concentration representative of twice the level found in the unspiked check sample or a level equal to 10 times the expected detection limit, whichever is greater. Prepare a spiking solution by dissolving the compounds in methylene chloride at the appropriate levels.

8.2.3 Spike a minimum of four aliquots of the check sample with the spiking solution to achieve the selected spike concentrations. Spike the samples after they have been transferred to centrifuge tubes for extraction. Analyze the spiked aliquots according to the method described beginning in Section 7.3.

8.2.4 Calculate the average percent recovery (R) and the standard deviation of the percent recovery (s) for all compounds and surrogate standards. Background corrections must be made before R and s calculations are performed. The average percent recovery must be greater than 20 for all compounds to be measured and greater than 60 for all surrogate compounds. The percent relative standard deviation of the percent recovery (s/R x 100) must be less than 20 for all compounds to be measured and all surrogate compounds.

8.3 The analyst must calculate method performance criteria for each of the surrogate standards.

8.3.1 Calculate upper and lower control limits for method performance for each surrogate standard, using the values for R and s calculated in Section 8.2.4:

Upper Control Limit (UCL) = R + 3s
Lower Control Limit (LCL) = R - 3s

The UCL and LCL can be used to construct control charts that are useful in observing trends in performance.

8.3.2 For each surrogate standard, the laboratory must maintain a record of the R and s values obtained for each surrogate standard in each waste sample analyzed. An accuracy statement should be prepared from these data and updated regularly.

8.4 The laboratory is required to spike all samples with the surrogate standard to monitor spike recoveries. The spiking level used should be that which will give a concentration in the final extract used for GC/MS analysis that is equal to the concentration of the internal standard assuming a 100% recovery of the surrogate standards. For unknown samples, the spiking level is determined by performing the extraction steps in Section 7.3 on a separate aliquot of the sample and calculating the amount of internal standard per gram of sample as described in Section 7.3.8. If the recovery for any surrogate standard does not fall within the control limits for method performance, the results reported for that sample must be qualified as being outside of control limits. The laboratory must monitor the frequency of data so qualified to ensure that it remains at or below 5%. Three surrogate standards, namely decafluorobiphenyl, 2-fluoroaniline, and pentafluorophenol, are recommended for general use to monitor recovery of neutral, basic, and acidic compounds, respectively.

8.5 Before processing any samples, the analyst must demonstrate through the analysis of a process blank that all glassware and reagent interferences are under control. Each time a set of samples is extracted or there is a change in reagents, a process blank should be analyzed to determine the level of laboratory contamination.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field replicates may be analyzed to monitor the precision of the sample technique. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance evaluation studies.

8.7 The features that must be monitored for each GC/MS analysis run for quality control purposes and for which performance criteria must be met are as follows:

- Relative ion abundances of the mass spectrometer tuning compound DFTPP.
- Response factors of column performance standards and retention time standards.
- Relative retention time of column performance standards and retention time standards.
- Peak area intensity of the internal standard, e.g., D_{10}-phenanthrene.

8.8 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be carried through all stages of sample preparation and measurement; they should be analyzed to validate the sensitivity and accuracy of the analysis. If the fortified waste samples do not indicate sufficient sensitivity to detect less than or equal to 1 µg/g of sample, then the sensitivity of the instrument should be increased or the extract subjected to additional cleanup. Detection limits to be used for groundwater samples are indicated in Tables 1 and 2. Where doubt exists over the identification of a peak on the chromatograph, confirmatory techniques such as mass spectroscopy should be used.

8.9 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in Tables 1 and 2 were obtained using reagent water. Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

8.10 In a single laboratory, using reagent water and wastewaters spiked at or near background levels, the average recoveries presented in Tables 4 and 5 were obtained. The standard deviation of the measurement in percent recovery is also included in Tables 4 and 5.

TABLE 4. ACCURACY AND PRECISION FOR BASE/NEUTRAL EXTRACTABLES

Parameter	Reagent water		Wastewater	
	Average percent recovery	Standard deviation (%)	Average percent recovery	Standard deviation (%)
Acenaphthene	77	23	83	29
Acenaphthylene	78	22	82	23
Aldrin	72	6	--	--
Anthracene	84	14	76	22
Benzo(a)anthracene	83	19	75	28
Benzo(b)fluoranthene	96	68	41	21
Benzo(k)fluoranthene	96	68	47	27
Benzo(ghi)perylene	80	45	68	40
Benzo(a)pyrene	90	22	43	21
Benzidine	87	61	63	55
Butyl benzyl phthalate	47	32	74	43
β-BHC	69	25	--	--
δ-BHC	56	18	--	--
Bis (2-chloroethoxy) methane	84	33	82	74
Bis (2-chloroethyl) ether	56	36	72	37
Bis (2-chloroisopropyl) ether	71	33	71	39
Bis (2-ethylhexyl) phthalate	129	50	82	63
4-Bromophenyl phenyl ether	80	17	75	20
2-Chloronaphthalene	73	24	79	27
4-Chlorophenyl phenyl ether	45	11	--	--
Chrysene	83	19	75	28
4,4'-DDD	80	9	--	--
4,4'-DDE	69	20	--	--
4,4'-DDT	63	15	--	--
Dibenzo(a,h)anthracene	82	39	70	40
Di-n-butyl phthalate	70	25	93	51
1,2-Dichlorobenzene	59	27	62	28
1,3-Dichlorobenzene	55	28	54	24
1,4-Dichlorobenzene	61	31	63	35
3,3-Dichlorobenzidine	184	174	143	145
Diethyl phthalate	42	28	48	28
Dimethyl phthalate	25	33	35	36
2,4-Dinitrotoluene	83	32	79	34
2,6-Dinitrotoluene	79	18	79	25
Di-n-octylphthalate	97	37	89	62
Endosulfan sulfate	79	29	--	--
Fluoranthene	89	19	80	26
Fluorene	77	16	80	20
Heptachlor	69	6	--	--
Heptachlor epoxide	82	7	--	--

TABLE 4. (CONT.)

Parameter	Reagent water		Wastewater	
	Average percent recovery	Standard deviation (%)	Average percent recovery	Standard deviation (%)
Hexachlorobenzene	79	20	71	22
Hexachlorobutadiene	46	25	48	28
Hexachlorocyclopentadiene	27	25	12	12
Hexachloroethane	46	21	52	26
Indeno (1,2,3-cd) pyrene	65	37	81	43
Isophorone	75	33	77	42
Naphthalene	67	32	75	35
Nitrobenzene	72	31	82	54
N-Nitrosodi-n-propylamine	68	39	76	45
N-Nitrosodiphenylamine	84	24	86	31
PCB-1221	77	11	--	--
PCB-1254	80	13	--	--
Phenanthrene	84	14	76	22
Pyrene	86	15	80	23
1,2,4-Trichlorobenzene	64	16	69	26

Spiked between 5 and 2400 µg/l.

TABLE 5. ACCURACY AND PRECISION FOR ACID EXTRACTABLES

Parameter	Reagent water		Wastewater	
	Average percent recovery	Standard deviation (%)	Average percent recovery	Standard deviation (%)
4-Chloro-3-methylphenol	79	18	75	21
2-Chlorophenol	70	23	71	25
2,4-Dichlorophenol	74	24	80	21
2,4-Dimethylphenol	64	25	58	26
2,4-Dinitrophenol	78	21	108	56
2-Methyl-4,6-dinitrophenol	83	18	90	35
4-Nitrophenol	41	20	43	16
2-Nitrophenol	75	25	75	27
Pentachlorophenol	86	20	66	36
Phenol	36	14	36	21
2,4,6-Trichlorophenol	77	20	81	20

Spikes ranged from 10 to 1500 µg/l.